TITLE: ACTIVE CARBONATION: A NOVEL CONCEPT TO DEVELOP AN INTEGRATED CO_2 SEQUESTRATION MODULE FOR VISION 21 PLANTS

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GRANT NO.: DE-FG2601-NT41286

PERIOD OF PERFORMANCE: September, 2001 – March, 2002

DATE: April 1, 2002

1. ABSTRACT

Program Introduction: Rationale and Objective

Mineral carbonation, that involves the reaction of CO_2 with non-carbonate minerals to form stable mineral carbonates, has been recently proposed as a promising CO_2 sequestration technology due to the vast natural abundance of these raw minerals, the long term stability of the mineral carbonates formed, and the overall process being exothermic, and therefore, potentially economic viable. However, current mineral carbonation studies require extensive pulverization of the raw minerals, long reaction times (>6 hours) and extremely high partial pressures of CO_2 at >115 atm. Consequently, mineral carbonation will only become a viable cost-effective sequestration technology through innovative development of fast reaction routes under milder regimes in a continuous integrated process. The novel concept proposed here focuses on surface activation to accelerate the carbonation reaction efficiency. The overall objective of the proposed research program is the development of an active carbonation process that can ultimately evolve into an integrated CO_2 sequestration module for Vision 21 plants.

Accomplishments Achieved During the Current Period of Performance

During the current period of performance, September 2001 – March 2002, a selection of magnesium rich minerals, serpentine and olivine, have been used as carbonation feedstock materials. Surface activation studies have been conducted in these minerals to promote their inherent carbonation reactivity. The raw precursors and their activated materials have been studied by N_2 and CO_2 adsorption isotherms, thermogravimetric studies, optical and electronic microscopy, and X-ray diffraction to characterize their surface properties and assess their potential as carbonation minerals.

Adsorption isotherms (N_2-77K) conducted on the raw and treated serpentine samples showed that the adsorbed volume increases significantly for the activated samples compared to that of the raw serpentine sample, indicating that the activation process has increased the porosity of the activated samples. The BET surface area went up at least one order of magnitude to

142-330 m^2/g for the activated serpentines, compared to only ~16m^2/g for the raw material. For the activated serpentines, the adsorbed volume increases rapidly at low relative pressure, but it keeps increasing progressively, and there is a distinct hysteresis loop in the isotherm, which indicates that the sample porosity is a mixture of micropores (<2nm in width) and mesopores (2-50nm in width). Further porosity analysis have shown that after activation, the micropore surface area increased from 2m^2/g for the raw serpentine to 99-267m^2/g for the activated samples, and the average pore size decreased from 6.8nm for the raw serpentine to 3.0-3.4nm for the activated samples. CO_2 adsorption isotherms at 277K were also conducted on one of the activated serpentine samples and the raw sample, and the Langmuir reported surface area of the activated serpentine was 242m^2/g, compared to only 9m^2/g for the raw sample. Therefore, compared to the raw serpentine, the activated samples have developed significant microposity.

SEM studies showed that at the same magnification level, the activated sample presented more needle-like particles than the raw material. Images taken at greater magnification level showed that the structure of the activated serpentine had been significantly altered. In cooperation with the Mineral Sequestration group at NETL, mineral carbonation tests for the parent and one of the activated samples were conducted using 1-liter Hastelloy C-2000 continuous-stirred-tank-reactor (CSTR). XRD studies showed that some of the MgO was removed during the activation process, and this can be detrimental for the use of the activated serpentine as feedstock for carbon sequestration. Thermogravimetric analysis in N_2 and CO_2 were also conducted on the parent serpentine and its activated counterparts from room temperature to 850°C. The parent serpentine lost around 15wt%, while the activated samples only lost 7-11wt%. The weight loss is known to be associated with water removal. Furthermore, the weight loss of the activated serpentines was shifted to higher temperatures than those reported for the parent sample. This indicated that the activation process acted selectively removing low-temperature (< 600°C) hydroxyl groups.

Plans for the Remaining Period of Performance

The work planned for the remaining months of Phase-I of this research program include the following tasks:

- Continue the activation of the serpentine and olivine samples under a wider range of controlled operating variables in order to establish the optimum route for the generation of activated carbonation minerals.
- Integrated carbonation studies on the raw materials and their activated counterparts as well as carbonation experiments will also be conducted using in-situ thermogravimetric analyses to determine reaction kinetics.
- A preliminary economic assessment will be performed to evaluate the economic viability of the proposed active carbonation concept as an integrated on-line CO_2 scrubber.
- Publish the outcome of these investigations.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference Presentations

- Study of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration, M. M. Maroto-Valer, D. J. Fauth, M. E. Kuchta, Y. Zhang, J. M. Andrésen, and Y. Soong, 18th Annual International Pittsburgh Coal Conference, 2001, CD-publication: 23-01.pdf.
- Integrated carbonation: a novel concept to develop a CO_2 sequestration module for power plants, M. M. Maroto-Valer, M. E. Kuchta, Y. Zhang, and J. M. Andrésen, Sixth International Conference on Greenhouse Gas Control Technologies, 2002, Submitted.
- Activation of serpentine and olivine minerals for enhanced CO_2 sequestration, M. E. Kuchta, Y. Zhang, M. M. Maroto-Valer, and J. M. Andrésen, 19th Annual International Pittsburgh Coal Conference, 2002, Submitted.

Students Supported Under this Grant

- Matthew E. Kuchta, graduate student in the Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University.